

THE DISTRIBUTION OF SOLUTES IN SILICA GEL

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
SUTTON REDFERN

BALTIMORE
1936



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THE DISTRIBUTION OF SOLUTES IN SILICA GEL

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It has been shown that within a hydrogel of silicic acid a solute is associated with a greater quantity of water than outside the hydrogel. If the concentrations are expressed as molalities, then it is found that the concentration inside the gel is less than the concentration outside. This conclusion was reached on the basis of the experimental studies of the diffusion of electrolytes in hydrogels by Allan (1) and the analytical studies of Love (7). These papers gave results for sodium sulfate and hydrochloric acid.

Allan and Love were also led to believe that the activity coefficient of the solute in the gel was different from the activity coefficient outside, since the activities at equilibrium must be equal. However, this conclusion is based on the assumption that all of the water in the gel is acting in the rôle of solvent. This is probably not true, because there is considerable evidence for the existence of what is called bound water. The hydration of molecules or ions in solution is one example. Substances such as gelatin, gum arabic, silica gel, and alumina have the property of adsorbing water. This water does not exhibit its normal vapor pressure or other colligative properties. Neuhausen and Patrick (11) have shown that a silica gel can be heated to 300°C. in a vacuum produced by a Gaede pump for a period of 6 hours without reducing the water content below 4.8 per cent. In recent years the extensive series of measurements of bound water initiated by the studies of Newton and Gortner (12) on bound water in plant saps leave little doubt that such a thing as bound water exists.

A satisfactory, absolute definition of bound water has never been made. Briggs (2) says that "there are nearly as many definitions of bound water as there are methods for determining it. The methods are consistent in that they remove or otherwise change the state of a fraction of the water leaving a portion unaccounted for, this being designated as bound. The

usual idea of bound water carries with it a picture of a portion of the water in the system as being associated with the colloid phase with such strength that it is no longer free to exhibit those properties which are characteristic of water, i.e. it is no longer available to act as a solvent, or it cannot be separated from the colloid by freezing it or by subjecting the system to pressure, as in an ultrafilter."

Very probably there is a definite bound water $\rightleftharpoons$ free water equilibrium which is measured at a different point in each different method. This makes it difficult to get check results, although Sayre (15) has obtained check results by three different methods on a gum arabic sol.

The purpose of this study is to test accurately the whole question from an experimental standpoint, and furthermore to formulate if possible a rational explanation of the phenomena involved.

BRIEF STATEMENT OF METHOD

The method of studying the distribution of the various solutes between the gel and its surrounding equilibrium solution is in brief as follows: A cylinder of silica gel, of previously determined water content, was placed in a flask with the desired solute solution; the flask was placed in the thermostat and allowed to stand, with occasional shaking, for two weeks or longer. Then duplicate samples of the external solution were removed to tared weighing bottles, and the molal concentration of the solute determined by the appropriate method. The gel was removed from the solution and carefully wiped with filter paper to remove any excess solution. Four samples of the gel were then cut off and the silicon dioxide content of two of them and the solute content of the other two were determined. The above analyses gave sufficient data from which the concentration of solute in the gel and the concentration of solute in the external solution could be calculated.

PREPARATION OF GELS

Gels prepared from sulfurous acid (1) have a greater mechanical strength than gels prepared from sulfuric or hydrochloric acids and so were used. The sodium silicate used to prepare the gels was a commercial product containing Na_2O and SiO_2 in the ratio 1:3.51. It was diluted until it contained 6 per cent Na_2O . The gels were prepared by adding the diluted sodium silicate solution to a saturated aqueous solution of sulfur dioxide and pouring the resulting sol into paraffined glass molds 3.4×10 cm. After the sol set to a gel, it was removed and washed overnight in tap water in order to remove most of the soluble salts. The gel cylinders were then washed alternately in 6 *N* and 12 *N* hydrochloric acid until no more iron was extracted, and finally washed in distilled water until free of chloride. Gels washed in this manner with hydrochloric acid did not

contain more than 0.1 per cent residue based on the weight of silica after the silica was removed with hydrofluoric acid and sulfuric acid.

After being washed, the gels were dried superficially in the open air. They were now approximately 85 per cent water and could be used directly as representing this water content. For lower water contents, the gel cylinders were dried slowly under raised bell jars. The drying process was followed by weighing the cylinders. Since these dried gels would crack when placed in water, they were resaturated with water vapor by Allan's method (1).

EQUILIBRATION AND SAMPLING OF GELS

The solutes used in this investigation were potassium chloride, potassium bromide, sodium chloride, sodium bromide, lithium chloride, magnesium chloride, barium chloride, calcium chloride, strontium chloride, and dextrose. These solutes were all of c.p. grade and were used without further purification.

A gel cylinder was placed in a 250-ml. wide-mouth Erlenmeyer flask and covered with a solution of the solute. The flask was tightly stoppered with a rubber stopper, placed in a thermostat maintained at $25.00^{\circ}\text{C} \pm 0.05^{\circ}$, and left for two weeks or longer. The dextrose solutions were covered with a layer of toluene to prevent the formation of mold. It is a safe assumption that the toluene did not interfere. Jones and Gortner (5) also used toluene "because of its inactivity towards aqueous colloidal systems." When the gel had come to equilibrium, duplicate samples of the external solution were removed, weighed, and the amount of dissolved solute determined. The gel cylinder was then removed and immediately wiped off carefully with filter paper. Two samples of gel were then broken off with a knife and placed in weighing bottles. The silica was determined in these samples. The rest of the gel was split into two pieces, and the solute removed and analyzed by an appropriate method.

METHODS OF EXTRACTION AND ANALYSIS

The gel samples were extracted in a Soxhlet extraction apparatus. When dextrose was extracted with boiling water, a slight decomposition took place. Therefore the extraction apparatus was modified so that it could be run under a constant reduced pressure of 80 mm. of mercury. The lowered boiling point prevented decomposition. Difficulty was experienced with bumping under the reduced pressure, so a slow stream of nitrogen was introduced through a tube sealed through the side of the flask. A water pump supplied the necessary vacuum.

The Mohr method was used for the analysis of all the electrolytes except barium chloride; in this case the Volhard method was used. The dextrose was analyzed by the Quisumbing and Thomas (14) modification of Feh-

ling's method. Silica was determined by the Willard and Cake (20) perchloric acid method. It was not necessary to go through this procedure for the samples containing dextrose. In this case the gel was weighed directly into a platinum crucible and ignited.

The initial water content of each gel cylinder was determined before it was placed in the solution. Duplicate samples of the resaturated gel were removed from each end of the cylinder, placed in platinum crucibles, and ignited.

CALCULATIONS

The analysis of the equilibrium solution and the gel gave the following ratios:

$$A = \frac{\text{Solute}}{\text{H}_2\text{O in solution}} \quad B = \frac{\text{Solute}}{\text{Gel}} \quad C = \frac{\text{SiO}_2}{\text{Gel}}$$

These ratios, of course, are expressed as grams per gram. By calculation the following ratios were obtained:

$$D = \frac{\text{H}_2\text{O}}{\text{Gel}} = 1 - (B + C) \quad E = \frac{\text{Solute}}{\text{H}_2\text{O in gel}} = \frac{B}{D} \quad \Delta = A - E$$

The Δ is the difference between the concentration outside and inside and is found to be always positive.

If the free water of the system is defined as the fraction of the total water which is acting as a solvent and gives a solution inside the gel of the same concentration as the surrounding equilibrium solution, then the bound water is defined as the difference between the total water and the free water. In general, all methods for determining bound water depend on the determination of the total and free water, and define the bound water by difference.

In order to apply the above definition, let X = the number of grams of bound water in 1 g. of gel. Then must

$$\frac{B}{D - X} = A$$

or

$$\frac{X}{D} = \frac{A - E}{A} = \frac{\Delta}{A}$$

but X/D is the fraction of the total water which is bound. However, a better expression of the amount of bound water is to give the number of grams of bound water per gram of silica. This ratio, called W , is given by

$$W = \frac{D \cdot \Delta}{C \cdot A} = \frac{\text{grams H}_2\text{O}}{\text{grams SiO}_2}$$

In order to see whether there was any correlation between the activity of the water in the equilibrium solution and the amount of bound water, the activity of the water in the different solutions was calculated from the activity coefficients of the solute by the following formula:

$$-\log a_{(m_1)} = \frac{m_1\nu}{127.84} + \frac{\nu}{55.51} \int_0^{m_1} m \, d \log \gamma$$

where $a_{(m_1)}$ = activity of water when the molality of the solute is m_1 ,

m_1 = molality of solute,

ν = total number of ions formed from solute, and

γ = activity coefficient of solute.

TABLE 1
85 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILI- BIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO ₂	ACTIVITY OF WATER	RATIO A/E
MgCl ₂	86.79	0.4231	0.00215	0.302	0.981	1.056
CaCl ₂	86.72	0.3990	0.00187	0.273	0.981	1.044
SrCl ₂	86.66	0.4043	0.00314	0.320	0.981	1.052
BaCl ₂	86.33	0.4190	0.00438	0.318	0.981	1.053
NaCl.....	86.89	0.8322	0.00168	0.231	0.973	1.036
NaBr.....	87.00	0.8264	0.00309	0.239	0.972	1.038
LiCl.....	88.29	0.8260	0.00107	0.228	0.971	1.032
KBr.....	88.22	0.8324	0.00253	0.187	0.973	1.026
KCl.....	84.06	0.8273	0.00181	0.160	0.974	1.030
KCl.....	84.06	0.4033	0.00095	0.175	0.987	1.033
Dextrose.....	82.68	0.8656	0.00660	0.201*	0.985	1.044
Dextrose.....	85.16	0.4227	0.00357	0.272	0.992	1.049

* These results deviate from the general rule that the amount of bound water decreases as the silica content of the gel increases.

By plotting m against $\log \gamma$, the last integral can be graphically integrated. The necessary values of the activity coefficients were taken from the Landolt-Börnstein (6) tables. The coefficients for magnesium chloride were at the freezing point of the solution, but it was assumed that these were not greatly different from the values at 25°C. The curves were carefully plotted and integrated with a polar planimeter. In the case of the dextrose solutions the activity of the water was calculated from the measurements of Morse (9) on the osmotic pressures of dextrose solutions.

DATA

All of the data on the gels can be conveniently divided into three groups, depending on the approximate initial water content of the gel. The three

groups are designated as the 85 per cent gel series, the 70 per cent gel series, and the 50 per cent gel series. Tables 1, 2, and 3 give the results

TABLE 2
70 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILI- BRIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO_2	ACTIVITY OF WATER	RATIO A/E
MgCl_2	73.02	0.5149	0.00444	0.263	0.973	1.100
CaCl_2	72.16	0.4557	0.00469	0.257	0.976	1.102
SrCl_2	71.35	0.4625	0.00818	0.300	0.978	1.126
BaCl_2	63.76	0.4864	0.01420	0.272	0.977	1.163
NaCl	72.40	0.9616	0.00441	0.218	0.968	1.085
NaBr	72.24	0.9422	0.00867	0.246*	0.968	1.098
LiCl	65.73	0.9642	0.00395	0.204*	0.966	1.107
KBr	67.15	0.9671	0.00980	0.178	0.969	1.093
KCl	65.93	0.9582	0.00477	0.141	0.970	1.072
KCl	70.94	0.4718	0.00267	0.197*	0.985	1.082
Dextrose.....	69.01	1.007	0.01660	0.210	0.982	1.101
Dextrose.....	72.84	0.4723	0.00712	0.233	0.992	1.091

* These results deviate from the general rule that the amount of bound water decreases as the silica content of the gel increases.

TABLE 3
50 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILI- BRIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO_2	ACTIVITY OF WATER	RATIO A/E
MgCl_2	50.69	0.5052	0.01062	0.240	0.974	1.283
CaCl_2	55.21	0.4741	0.00833	0.204	0.975	1.188
SrCl_2	54.04	0.4877	0.01575	0.256	0.977	1.256
BaCl_2	54.10	0.4888	0.02010	0.244	0.977	1.246
NaCl	54.62	0.9996	0.00933	0.202	0.967	1.190
NaBr	54.19	0.9912	0.01620	0.198	0.966	1.189
LiCl	55.88	0.9800	0.00653	0.208	0.965	1.186
KBr	54.61	0.9990	0.01440	0.150	0.968	1.138
KCl	55.46	0.9962	0.00776	0.135	0.968	1.117
KCl	55.31	0.4899	0.00420	0.155	0.984	1.130
Dextrose.....	53.78	1.056	0.03450	0.205	0.981	1.222
Dextrose.....	52.94	0.5033	0.01670	0.212	0.991	1.226

for the respective series. Calculations were also made assuming that the dextrose molecule is monohydrated in solution. It was found that the formation of a monohydrate increases the difference in concentrations

outside and inside. These calculations are not tabulated, because the only evidence for the hydration of dextrose is the fact that dextrose forms a crystalline monohydrate. Sucrose in dilute solutions forms a hexahydrate (16), and Newton and Gortner (12) always corrected their freezing-point measurements by assuming the formation of the sucrose hexahydrate.

The accuracy of the determinations is as follows: In the determination of the water content of the gels, the maximum deviation from the mean was ± 0.5 per cent. The deviation from the mean of ratio *A* was ± 0.2 per cent; of ratio *B*, ± 1.0 per cent; and of ratio *C*, ± 0.75 per cent. It is therefore believed that the results are accurate to at least ± 2.0 per cent.

DISCUSSION

According to a tentative theory of one of the authors, it was originally expected that the dextrose would be equally distributed. This expectation was pointed out to Dr. I. Langmuir in the spring of 1935; he immediately suggested that the electrolytes showed a difference because the dielectric constant inside the gel was different from that in the outside solution. This would mean a difference in the electrical energy of the ions and a Boltzmann distribution would result. However, the experimental results showed that this suggestion was not the explanation. Furthermore, the idea that the dielectric constant of the largest fraction of the water in the gel is different from the water outside is probably not true. Marinesco (8) measured the dielectric constant of aqueous solutions of hydrophilic colloids, and by application of the dipole theory of Debye determined the quantity of water fixed by these colloids. In effect free water has a dielectric constant of 80, while in the water which is bound by colloids the molecular dipoles are blocked and can no longer lead to polarization, so that the dielectric constant is now no more than of the order of 2 to 3. Other evidence for a lower dielectric constant of the bound water is to be found in the literature (10, 17, 18, 19).

The calculations made on the assumption of bound water show definite qualitative trends, although no quantitative results can be deduced from the present set of measurements. The data show that in all cases except four, which are starred, the amount of bound water decreases as the silica content of the gel increases. This decrease is easily explained qualitatively. The gel cylinders when dried shrink considerably in volume and this shrinkage is irreversible. Therefore the gels of lower water content have a smaller internal volume, which means less surface for the layer or layers of bound water; consequently there is less bound water per gram of silica.

The same results were found for gelatin gels and sols by Jones and Gortner (5) using the dilatometric method and by Newton and Martin (13) using the cryoscopic method. In the gelatin-water system, however,

the water binding appears to be an adsorption reaction, because a logarithmic relationship was found to exist between the concentration of the gelatin gel and the grams of water which were bound per gram of dry gelatin. An attempt was made to plot the present results on log-log coördinate paper, but the measurements did not give a straight line.

Briggs (2) found that the amount of bound water associated with the colloid varied with the activity of the water. The higher the activity of the water, the greater the quantity of bound water. Measurements of the gum arabic-water systems with the cryoscopic technique showed that different solutes gave a smooth curve of water content against water activity.

The results on silica gel do not show any such simple relations. For example, an examination of the results for magnesium chloride, calcium chloride, strontium chloride, and barium chloride in the 85 per cent gel series shows different values for the amount of bound water, although the activity of the water is the same for each salt. The water contents of the different gels are sufficiently close to remove this variable. However, in the case where the same solute was used, potassium chloride or dextrose, the bound water is greater the greater the activity of the water. Apparently Briggs' statement—"At any given activity of the water in a system in which colloids and crystalloids are in equilibrium, provided the various non-water components have not reacted with each other upon mixing, the amount of water associated with or bound by a given weight of any of the non-water components will always be the same, and it will be the same as that which the given weight of the component will be associated at the same water activity when it is the only non-water component in equilibrium with water."—is not true for the silica systems.

It was thought that perhaps a Donnan equilibrium was responsible for the unequal distribution. The Donnan equilibria are characterized by the presence in a system of electrolytes of a species of ion which is restrained in *any* way from diffusing to all parts of the system, and this gives rise to unequal distribution of every species of diffusible ion present. These equilibria are immediately thrown out because of the experimentally determined unequal distribution of dextrose, and also because the same distribution would be expected for all the uni-univalent chlorides and the same for all the bi-univalent chlorides; the latter is found not to be true. Furthermore, it is hard to find the restraint necessary for the distribution.

Adsorption also will not explain the results. Grettie and Williams (4) found that even activated silica, i.e., silica which had been heated to 120° C. for several hours, only adsorbed dextrose to the extent of 0.7 per cent. The silica gel used in the present experiments was certainly not activated and would be expected to show no adsorption. However, adsorption is in the opposite direction to that which was actually found. If the gel does adsorb chloride ions, as was found by Ganguly and Krishnamurti (3)

for a silica sol prepared from silicon tetrachloride, then this would also produce the opposite effect, namely, a greater concentration inside the gel than outside.

It is frankly admitted that at present the authors cannot suggest a reasonably satisfactory explanation of the results described herein.

SUMMARY

1. A study has been made of the distribution of potassium chloride, potassium bromide, sodium chloride, sodium bromide, lithium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride, and dextrose between a hydrogel of silicic acid and the surrounding equilibrium solution.

2. In all cases the molal concentration of solute inside the gel was found to be less than the molal concentration outside.

3. Calculations made on the assumption that part of the water was not acting as a solvent but was bound water showed that the amount of bound water decreased as the silica content of the gel increased.

4. No correlation was found between the activity of the water and the quantity of bound water.

5. The results could not be explained satisfactorily on the basis of bound water, adsorption, or Donnan equilibria.

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BIOGRAPHY

Sutton Redfern, the author of this dissertation, was born in Seattle, Washington, on April 18, 1912. He received his elementary education in the John Hay public school and graduated from Queen Anne High School in 1929. In the fall of 1929 he entered the University of Washington and received a B.S. degree in chemistry in 1933. He was awarded the Fleischmann Fellowship from the State of Washington and entered the Johns Hopkins University as a graduate student of chemistry in the fall of 1933. He was employed by the Fleischmann Laboratories during the summers of 1934 and 1935.

